Equivalent formulations of the generalized pericyclic selection rules

There are two distinct sets of criteria, both commonly referred to as the generalized pericyclic selection rules (or generalized Woodward–Hoffmann rules), for determining whether a pericyclic reaction (of any class) is allowed or forbidden. On casual inspection, it is not obvious that these formulations of the generalized pericyclic selection rules are equivalent in the sense that they must reach the same conclusion for every conceivable pericyclic process. Here, we present a rigorous demonstration of this equivalence by introducing a formalism to convert the original statement of equivalence, expressed in chemical terms, to a purely arithmetic proposition, the proof of which is straightforward.

Proposition 1. *The following formulations of the generalized pericyclic selection rules are equivalent:*[1]

A: ('Componentwise') A pericyclic process under thermal conditions is allowed if and only if the sum of the number of suprafacial $4q+2$ *components and antarafacial* $4r$ *components is odd.*

B: ('Global') A pericyclic process under thermal conditions is allowed if and only if the total electron count is $4n+2$ *and the number of antarafacial components is even or the total electron count is* $4n$ *and the number of antarafacial components is odd.*[2]

Proof. As we will argue in the following paragraphs, Proposition 1 is equivalent to Proposition 2, whose proof is given below. □

We begin by defining a set of symbols that encode the electron count and the orbital interaction topology of each component in a way that tracks and preserves parity (odd / even) relationships. In particular, we assign a k-component pericyclic reaction a set of ordered triples $\{(n_1, f_1, 1), \ldots, (n_k, f_k, k)\}$ by associating component i with 'symbol' (n_i, f_i, i) according to the following rules:[3]

$$n_i = \begin{cases} 0 & \text{if } i \text{ is a } 4r \text{ component} \\ 1 & \text{if } i \text{ is a } 4q+2 \text{ component,} \end{cases}$$

and

$$f_i = \begin{cases} 0 & \text{if } i \text{ is suprafacial} \\ 1 & \text{if } i \text{ is antarafacial.} \end{cases}$$

Examples:
(1) The conrotatory 4 e^- ring opening of cyclobutene ($[_\sigma 2_\mathrm{a} + _\pi 2_\mathrm{s}]$) is assigned $\{(1,1,1),(1,0,2)\}$.
(2) The conrotatory 8 e^- ring closing of octatetraene ($[_\pi 8_\mathrm{a}]$) is assigned $\{(0,1,1)\}$.
(3) The Diels-Alder reaction ($[_\pi 2_\mathrm{s} + _\pi 4_\mathrm{s}]$) is assigned $\{(1,0,1),(0,0,2)\}$.
(4) The Alder ene reaction ($[_\pi 2_\mathrm{s} + _\sigma 2_\mathrm{s} + _\pi 2_\mathrm{s}]$) is assigned $\{(1,0,1),(1,0,2),(1,0,3)\}$.

For each component i, these rules establish one-to-one correspondences between the number of electrons modulo 4 ($4r/4q+2$) and n_i and between faciality (suprafacial / antarafacial) and f_i. The complete set of assigned symbols therefore contains all the information needed to determine whether a given pericyclic process is allowed or forbidden. Accordingly, we will reexpress Proposition 1 by translating criteria involving electron count and faciality into mathematical conditions involving n_i and f_i. We restate the criterion in the 'componentwise' formulation (A) as the condition "the number of symbols of the form $(1,0,i)$ or $(0,1,i)$ is odd," or equivalently, "the number of symbols such that $n_i \neq f_i$ is odd." To restate the 'global' formulation (B), we note that the total electron count of a pericyclic reaction is of the form $4n+2$ or $4n$ precisely when the number of $4q+2$ components is odd or even, respectively. Thus, we restate the criteria in B as the condition "$\sum_i n_i$ is odd and $\sum_i f_i$ is even, or $\sum_i n_i$ is even and $\sum_i f_i$ is odd," or more succinctly, "exactly one of the sums $\sum_i n_i, \sum_i f_i$ is odd," where $\sum_i$ is shorthand for $\sum_{i=1}^{k}$. Putting everything together, we obtain the following:

Proposition 2. *Let* $S = \{(n_1, f_1, 1), \cdots, (n_k, f_k, k)\}$ *be a set of symbols with* $n_i, f_i \in \{0,1\}$. *Then the number of symbols in* S *such that* $n_i \neq f_i$ *is odd if and only if exactly one of the sums* $\sum_i n_i, \sum_i f_i$ *is odd.*

Proof. We first note that $\sum_i n_i$ or $\sum_i f_i$ is odd, but not both, if and only if $\sum_i n_i + f_i$ is odd. Thus, it suffices to show that $\sum_i n_i + f_i$ and the number of symbols in S such that $n_i \neq f_i$ have the same parity. We observe that any element of S such that $n_i = f_i$ can be omitted from the aforementioned sum without changing its parity, since $n_i = f_i \iff n_i + f_i = 0 \text{ or } 2 \equiv 0 \pmod 2$.[4] On the other hand, $n_i \neq f_i \iff n_i + f_i = 1$, so

$$\sum_i n_i + f_i \equiv \sum_{n_i \neq f_i} n_i + f_i = \sum_{n_i \neq f_i} 1 \pmod 2.$$

Since $\sum_{n_i \neq f_i} 1$ is an expression for the number of symbols in S such that $n_i \neq f_i$, the proof is complete. □

[1] The 'componentwise' formulation was proposed by Woodward and Hoffmann in *ACIEE* **1969**, *8*, 781. Because the number of antarafacial components and the number of phase inversions (for any choice of basis orbitals) have the same parity, the 'global' formulation can be regarded as a reframing of the Dewar–Zimmerman aromatic transition state theory (Hückel *vs.* Möbius topology) using Woodward–Hoffmann terminology; see *JACS* **1966**, *88*, 1563; *Tetrahedron* **1966**, *Suppl. 8*, 75.

[2] *Mnemonic:* A thermal pericyclic reaction involving P electron pairs and A antarafacial components is allowed if and only if $P + A$ is odd.

[3] The index i chosen to represent a particular component is unimportant, provided a distinct value is assigned to each one.

[4] The symbol $\iff$ means 'if and only if.' The notation $u \equiv v \pmod j$ means j divides $u - v$. Thus $u \equiv v \pmod 2$ means u, v have the same parity.